Reactivity Improvement of Bamboo Dissolving Pulp by Xylanase Modification

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A high reactivity is an essential prerequisite for dissolving pulp. In this study, xylanase modification to increase the reactivity of bamboo dissolving pulp was investigated. The original reactivity of a bamboo dissolving pulp prepared by a prehydrolysis kraft pulping process and bleached by (OP)-H-P (oxygen delignification enhanced with peroxide - sodium hypochlorite - peroxide) is very low. The reactivity of the pulp was increased drastically after xylanase modification, which lowered the pulp's pentosan content. Simultaneously, the crystallinity index of the dissolving pulp decreased slightly after xylanase modification. The microscopic appearance of the fiber surfaces changed slightly. The average curl and kink indices were lower at a xylanase charge of 1.0 IU/g compared to the other charges, while changes to the yield loss and the degree of polymerization were negligible. The mechanism for the increased pulp reactivity is discussed.

INTRODUCTION

Dissolving pulps are chemically refined bleached pulps that are composed of over 90% pure cellulose. In view of making dissolving pulp, researchers have embarked on the development of new technologies for the utilization of raw lignocellulosic materials, such as cotton linter, aspen wood, jute stem, bagasse, masson pine, and bamboo (Helmy and State 1991; Abad *et al.* 2000; Xu and Jiang 2005; Jahan 2009; Li and Ma 2009; Liu and Xue 2013). Traditionally, there are basically two processes for the production of dissolving pulp. These include extensive acid sulfite cooking (Sixta *et al.* 2004) and prehydrolysis-sulfate (kraft) cooking (Saeed *et al.* 2012). The basic idea in both processes is to remove as much hemicellulose as possible from the cellulose fibers, followed by delignification, to obtain a high content of alpha cellulose. This is essential because the various end uses of dissolving pulp do not tolerate short-chained hemicelluloses with variable substituent pendant groups, which can drastically decrease the reactivity of the resulting dissolving pulp.

The reactivity of dissolving pulps towards derivatization or dissolution is a crucial quality parameter and is primarily determined by the accessibility of the hydroxyl groups. Generally, a highly reactive dissolving pulp is difficult to obtain by just increasing the alpha cellulose content, which can dramatically decrease the dissolving pulp yield. Therefore, attention has shifted to nitren and hot water extraction (Janzon *et al.* 2008; Borrega *et al.* 2013), or enzymatic modification to facilitate the accessibility of chemicals to the cellulose. Five commercial cellulases have been tested to increase the reactivity of a dissolving pulp for viscose preparation (Kvarnlof *et al.* 2006). Endoglucanase treatment

can further increase both the amount of xylan and mannan solubilized from softwood sulfite dissolving pulps (Gubitz *et al.* 1997). Endoglucanase activity might lead to swelling of the cell wall, leading to increased exposure of the dissolving pulp cellulose to solvents and reagents (Henriksson *et al.* 2005; Engstrom *et al.* 2006). An alkali extraction step after xylanase treatment and followed by endoglucanase treatment as a final step can significantly reduce the hemicellulose content and increase the reactivity of the pulp (Kaya *et al.* 1995; Kopcke *et al.* 2008). Xylanase treatment followed by cold alkaline extraction and a final endoglucanase treatment can upgrade non-wood paper-grade pulps to dissolving-grade pulps for viscose production (Ibarra *et al.* 2010). In addition, enzyme treatments have been performed on *Eucalyptus globulus* dissolving pulp for viscose application; and the results indicated that the xylanase pretreatment can increase the reactivity of the eucalypt pulp toward xanthation (Gehmayr *et al.* 2011). The amount of pentosan removal is mostly dependent on the enzyme charge of the treatment (Christov and Prior 1993, 1995; Christov *et al.* 1999).

Bamboo is a suitable lignocellulosic material for pulp and paper because its cellulose and hemicellulose contents are similar to those of other wood species (Salmela *et al.* 2008; Ribas Batalha *et al.* 2012). Bamboo, which is an abundant and renewable resource in China, can be used to produce dissolving pulp (Ma *et al.* 2011). However, bamboo dissolving pulps that have not been modified are difficult to process into high-quality viscose because of the pulp's low reactivity. There have been no studies carried out to explore the effect of xylanase modification on the reactivity of bamboo dissolving pulp. This communication considers the effects of xylanase modification on some properties of bamboo dissolving pulps in order to determine whether the removal of xylan opens up the nanostructure of the bamboo. It is proposed that such modified material is better exposed to chemicals during the subsequent viscose process. It is also expected that low-mass xylan left in the bamboo may decrease the quality of the bamboo dissolving pulp. Some selected properties, such as kappa number, pentosan content, α-cellulose content, degree of polymerization (DP), and reactivity, were investigated to characterize the effect of xylanase modification on the main properties of the dissolving pulps. It is expected that this study can shed light on the mechanisms by which xylanase modification of bamboo dissolving pulp can influence the pulp's quality.

EXPERIMENTAL

Materials

Bamboo dissolving pulp with a pentosan content of 3.42%, an *α*-cellulose content of 96.5%, a degree of polymerization of 502, a kappa number of 0.86, and a brightness of 85.6% ISO was produced in our laboratory based on optimized conditions disclosed in an earlier study (Wu *et al.* 2014). The xylanase (AU-PE89), which had an activity of 80,000 IU/g, was provided by Sukahan Biochemical Industry Co. Ltd.

Analytical Methods

Pentosan (TAPPI T223 cm-01, 2001), kappa number (TAPPI T236 om-99, 1999), *α*-cellulose (TAPPI T203 cm-99, 1999), and brightness values (TAPPI T525 om-12, 2012) were determined. The average degree of polymerization (DP) of pulp was determined and calculated (*i.e.*, $DP^{0.905} = 0.75 \cdot [\eta]$) from the intrinsic viscosity $[\eta]$, which was measured according to Chinese national standard FZ/T 50010.3 (2011). X-ray diffraction (XRD)

patterns of the pulp were recorded with an X'Pert diffraction instrument (D8-ADVANCE; Bruker, USA) using Cu radiation (λ = 0.15406 nm). Data were collected in the 5 to 50° range of 2θ with a 0.05° step every 1.5 s. The crystallinity index of the pulp was calculated using the method of Segal *et al.* (1959). Arithmetic fiber length and width, as well as curl and kink indices, of the pulps were determined by a fiber quality analyzer (OpTest, Canada) over the scale of 0 to 7.2 mm.

Reactivity Measurements

The reactivity of the dissolving pulps was determined *via* a two-step process in accordance with the Chinese national standard FZ/T 50010.13 (2011), which is based on the work by Wu *et al.* (2014). The lower the time value is, the higher the percentage of cellulose that reacted with the carbon disulfide; this indicates a higher reactivity of the dissolving pulp by the Fock method.

RESULTS AND DISCUSSION

The Effect of Xylanase Modification on the Reactivity of Bamboo Dissolving Pulp

Xylanase modification of the dissolving bamboo pulp was carried out at the optimal conditions of 50 °C, 60 min, 10% pulp consistency, and pH 5 (using sodium acetate buffer). The effects of different xylanase charges (IU/g oven-dried pulp) on reactivity and pentosan and α-cellulose contents of the pulp are shown in Table 1.

Xylanase modification had a very dramatic effect on the properties of the dissolving pulp. Although the initial α-cellulose content of the bamboo dissolving pulp was relatively high, its initial reactivity (Table 1) was very low. To achieve high reactivity levels comparable to wood or linter dissolving pulp, bamboo dissolving pulps need to be treated or activated. In the present study, the bamboo dissolving pulps were subjected to xylanase modification to improve the accessibility and reactivity of the pulps and to reduce the hemicellulose content. It was apparent that the xylanase modification could enhance the amount of hemicellulose removal and lower the pentosan content of bamboo dissolving pulp from 3.42% to below 3.0%. The reactivity was increased drastically after xylanase modification. It improved very rapidly at xylanase dosages between 0 and 1 IU/g; dosages higher than 1 IU/g afforded slightly lower reactivity when compared to the pulp treated with 1 IU/g. The α-cellulose content in the pulp remained relatively stable after the xylanase modification at various charges. Changes that occurred relative to the yield loss and the DP were minimal. Paice *et al.* (1988) reported that xylanase treatment causes the DP of pulp to increase slightly, which the authors suggested was caused by the partial hydrolysis and removal of low-DP xylans.

Table 1. Composition and Reactivity of Bamboo Dissolving Pulps Treated with Various Xylanase Charges

Xylanase charges (IU/g)	0	0.5	1.0	1.5	2.0	2.5
Yield (%)	100	99.34	99.45	98.89	98.45	98.24
Degree of polymerization (DP)	502	510	512	520	532	513
Pentosan (%)	3.42	3.50	3.13	2.97	2.86	2.75
α-cellulose (%)	96.5	96.9	97.6	96.9	96.7	96.5
Reactivity (s)	240.9	20.5	4.4	8.4	8.6	10.5

The Effect of Xylanase Modification on Morphology of Pulp Fiber

SEM images of the original bamboo dissolving pulp and the xylanase (1.0 IU/g) modified pulp are shown in Fig. 1. SEM results revealed that the surfaces of the bamboo dissolving pulp after xylanase modification became loose and had more cracks and gaps, the size of which was around 0.1μm to 0.5μm. The cracks and gaps were attributed to the dissolution of xylan (from 1.4 nm to 1.5 nm of its repeat unit length). These changes in fiber morphology created a favorable environment for the chemical penetration of carbon disulfide during the viscose process. In addition, xylanase modification probably resulted in moderate damage to the crystalline zone of fiber cells. Thus, the crystallinity index of bamboo dissolving pulp slightly changed, from 71.16% to 70.13%, as shown in Fig. 2.

The prehydrolysis kraft process for making bamboo dissolving pulps stabilizes residual hemicelluloses against further alkali attack during the viscose process. This lowers the reactivity of bamboo dissolving pulp and further prevents the production of acceptable quality bamboo dissolving pulps. Xylanase modification overcomes this problem, and the resulting dissolving pulp has a low level of pentosans. Obviously, the degree of polymerization of xylanase-modified bamboo dissolving pulp was also higher than that of the original pulp.
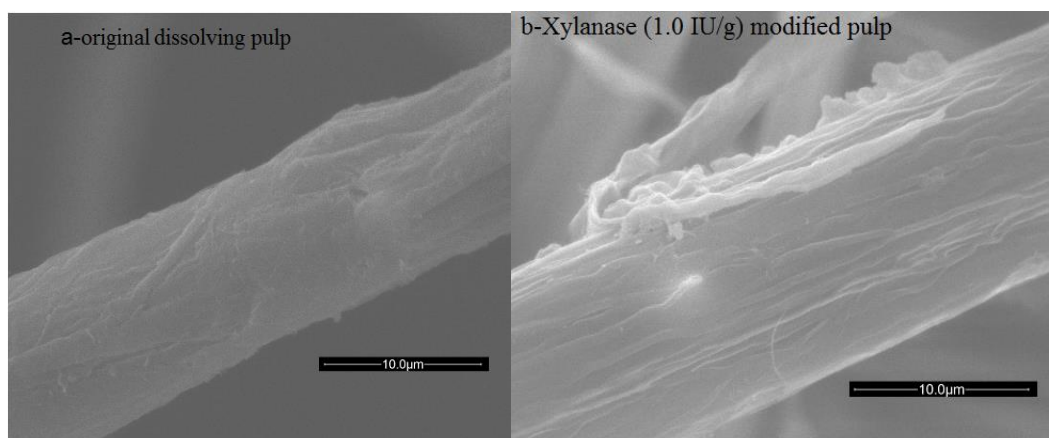

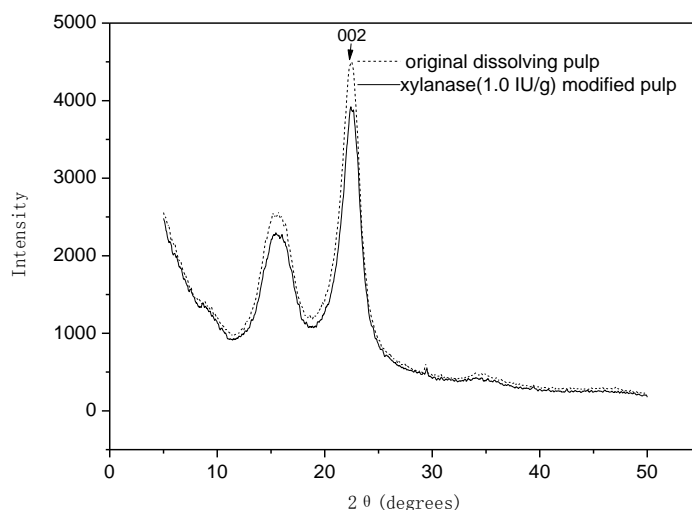**Fig. 1.** SEM images of bamboo dissolving pulp

Fig. 2. The X-ray diffractograms of bamboo dissolving pulp

The Effect of Xylanase Modification on Pulp Fiber Quality

The results in Table 2 showed that the changes to the average fiber length and width were negligible after xylanase modification. The average curl and kink indices were at their lowest values when 1.0 IU/g xylanase charge was used. This indicated that xylanase modification could possibly result in internal structural changes to the pulp fibers due to the removal of xylan.

Table 2. Changes to Bamboo Dissolving Pulp Fibers at Various Xylanase Charges

Xylanase charges (IU/g)	Average fiber length (mm)	Average fiber width (µm)	Curl index	Kink index
0	0.94	15.6	0.26	2.86
0.5	0.94	14.8	0.25	2.96
1.0	0.97	15.2	0.21	2.40
1.5	0.94	15.5	0.27	3.03
2.0	0.98	14.9	0.27	3.10
2.5	0.95	15.3	0.26	3.05

The Mechanism For Reactivity Improvement By Xylanase Modification

Several studies have proposed mechanisms to explain why xylanase treatment improves the reactivity of the pulp towards xanthanation. The first and simplest hypothesis is that the enzyme treatments cause a physical loosening of the fiber wall because of the partial depolymerization of the hemicellulose chains (Clark *et al.* 1991). The second hypothesis, which is well supported by experimental evidence, argues that the reprecipitated xylan, which is on the surface of fibers after kraft pulping, acts as a barrier to the extraction of residual lignin; xylanase treatments partially remove this xylan barrier (Kantelinen *et al.* 1993). In addition, using different techniques, it has been shown that internal structural changes occurred to the pulp fibers as a result of enzymatic action (Saake *et al*. 1995). Increasing the enzyme dosage also increases the accessible surface area by opening the macropores (Gronqvist *et al*. 2014) or nanopores (Penttila *et al*. 2010) of the fibers.

Based on our experimental data, one possible explanation for xylanase action in upgrading the bamboo dissolving pulp was that the dissolution of the hemicellulose by xylanase appeared to interrupt the connection between hemicellulose and cellulose in pulp. In addition, xylanase also likely led to moderate damage to the crystalline zone in the fiber cell, further improving the accessibility of carbon disulfide to the bamboo dissolving pulps for the viscose process. This xylanase coordination probably resulted in the rapid improvement of reactivity when the xylanase charge reached a certain value.

CONCLUSIONS

The reactivity of bamboo dissolving pulps, when subjected to xylanase modification, can improve by the reduction of their hemicellulose content. Furthermore, removal of xylan opens up the nanostructure of the bamboo such that fibers in the dissolving pulp are better exposed to carbon disulfide during the subsequent viscose process.

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